

THERMAL DESTRUCTION OF GEL COMPOSITIONS BASED ON ETHYL SILICATE AND BORIC ACID

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The physicochemical processes taking place in heat treatment of gel compositions with an additive of H_3BO_3 are considered. The phase composition of the heat treatment products is studied. The synthesis of oxygen-free SiC and B_4C compounds in heat treatment of sol-gel compositions in a reducing medium is identified.

The properties of the products obtained using a technology with elements of the sol-gel process significantly exceed the properties of the articles produced by the standard technology [1]. An important role is played by the choice of the binder which determines the binding capacity in molding of the crude articles, their strengthening in heat treatment, the participation of their components in the synthesis of new refractory compounds and the formation of the prescribed phase composition and structure.

A special role in the technology of refractories is played by binders based on ethyl silicate [2]. A promising method in using such binders consists in introduction of sintering and modifying additives in the mixture, i.e., production of a combined binder whose components intensify sintering of high-melting powders and act as sources for newly formed components.

The B_2O_3 additive in ceramic technology is traditionally used to decrease the sintering temperature [3]. Introduction of B^{3+} decreases the temperature of melt formation in silicon-containing materials and the emergence of coordination polyhedrons, facilitating breaking of the $Si-O-Si$ bond, which creates the conditions for emergence of $S-O-B$ bonds [4] with subsequent replacement of B^{3+} with the cations of the metals present in the raw material. This is one of the basic factors determining the subsequent phase formation in the heat treatment of the materials and products.

The purpose of the present study is to investigate the physicochemical processes taking place in heat treatment of ethyl silicate (ETS) – H_3BO_3 compositions.

The H_3BO_3 additive was introduced in the hydrolyzate in the course of hydrolysis of ETS-32 ethyl silicate with acid aqueous solution without organic solvents. HCl usually acted as the hydrolysis catalyst.

The hydrolysis processes and the physicochemical transformation in heat treatment were studied using the methods of IR spectroscopy, x-ray phase, differential thermal, and petrographic analysis.

Infrared spectroscopy was performed on a UR-20 spectrophotometer in the range of $400 - 4000\text{ cm}^{-1}$ (with KBr as the reference standard), x-ray phase analysis was carried out on a DRON-3M diffractometer (CuK_{α} -radiation), differential thermal analysis on a OD-103 derivatograph in air with a temperature elevation rate of $10^{\circ}\text{C}/\text{min}$, the petrographic analysis was performed with a MIN-8 microscope, and the x-ray phase analysis *in situ* was carried out on a DRON-2M diffractometer.

The IR-analysis of the gels in which concentrated HCl (0.8%, here and elsewhere wt.% is denoted unless otherwise specified) served as the basic catalyst for ethyl silicate hydrolysis and an additive of weak H_3BO_4 acid (0.2 – 4.0%) was present as well, revealed that the gel-forming process of the considered composition differed from the gel-forming processes in the hydrolyzates in which HCl was the only catalyst (Fig. 1). When H_3BO_4 (above 4%) is used as the hydrolysis catalyst, increased amorphization of silica is observed in the product of the combined hydrolyzate polycondensation.

According to the DTA data, introduction of even a small quantity of H_3BO_4 in the hydrolyzate of ETS-32 with HCl acting as the hydrolysis catalyst modifies the course of thermal oxidizing destruction of the gel (Fig. 2). Introduction of boric acid smoothes or causes the disappearance of the exothermic peaks typical of pure ethyl silicate gel up to temperatures of 663 K. The number of exothermic effects in the DTA curves of gels with a different content of H_3BO_3 does not change, but the shape of the peaks and their height are altered, which is evidence of the intensity of the release of products of thermal oxidizing destruction of the ETS – H_3BO_3 .

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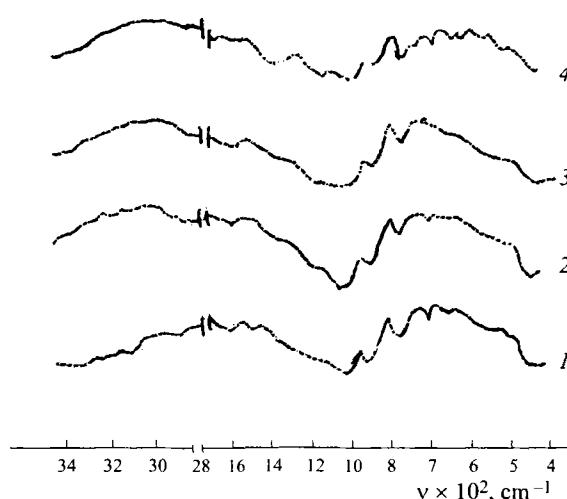


Fig. 1. IR spectra of ethyl silicate gels with HCl as strong hydrolysis catalyst (1) and with addition of H_3BO_3 (2–4). HCl content is 0.8% in all compositions; content of H_3BO_4 : 2) 0.2%; 3) 2.0%; 4) 4.0%.

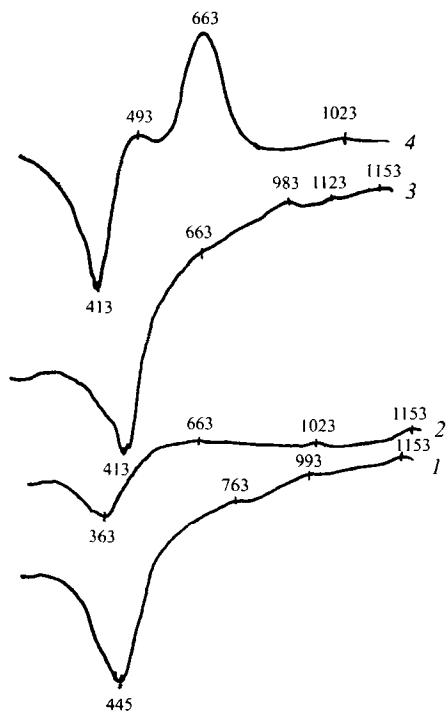


Fig. 2. DTA curves of gel compositions based on ethyl silicate: 1, 2, 3) with addition of 0.2, 2.0, and 4.0% H_3BO_3 , respectively; 4) without H_3BO_3 .

gel composition (up to 663 K) and the synthesis of new formations (983–1123 K).

The mass losses of gels with a different amount of H_3BO_4 additive in heat treatment are not equal (Fig. 3). With minimum introduction of H_3BO_3 (0.2%) in the ethyl silicate

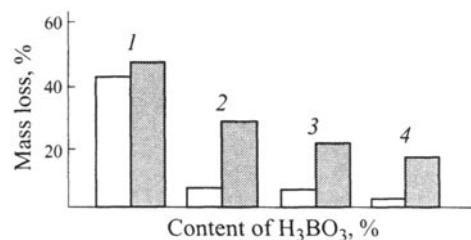


Fig. 3. Mass losses of ethyl silicate gels: 1) without H_3BO_3 , 2, 3, 4) with addition of 0.2, 2.0, and 4.0% H_3BO_3 , respectively; □) 763 K; ■) 1153 K.

binder, primary oxidation of the products of gel polyorganosiloxane thermal destruction occurs at the temperature of 763 K, and compared to the pure ethyl silicate binder, this oxidation process is shifted by 100 K to the right and its intensity sharply decreases. At the temperature of 763 K, the mass loss of the gel with boric acid is one-eighth to one-tenth of the mass loss occurring in heating of the pure gel. The mass losses in this case virtually do not depend on the amount of boric acid.

With an increase in the content of boric acid to 2.0%, the process of thermal destruction of the gel is delayed due to the emergence of a dense viscous melt in the composite. The steric bonds of the carbon-containing radicals which form clathrates in the SiO_2 cavities become stronger, the mass losses in heating decrease due to the fact that the boron-containing melt film reliably protects the carbon-containing clathrates from air oxygen. Moreover, with an increase in the amount of B_2O_3 in the melt, the protective properties improve, which is demonstrated by the study of the mass loss of the gel after heat treatment at 1153 K.

When 4.0% H_3BO_3 is added to the ethyl silicate binder, the thermal destruction products are virtually not oxidized in heating above 763 K. The complete disappearance of mass losses after heating at 963–1023 K can be explained by synthesis of new compounds from the components of the ETS– H_3BO_3 composition, which corresponds to the exothermic effects at the temperatures of 963 and 1023 K. The synthesis of new formations is confirmed by x-ray analysis.

Among the crystal phases of the gel of ETS– H_3BO_3 composition heat treated at 1273 K, x-ray analysis identified (Fig. 4) the high-temperature forms of quartz, cristobalite, tridymite, and silicon oxynitride. The amount of crystal phases formed at the specified firing temperature varies from 1 to 4%. The gel composition with H_3BO_3 (2.0%) produced 3% crystal phases, glass and 5–10% cryptophase (Table 1). The peak with $d = 3.18 \text{ \AA}$ in the diffraction pattern of the heat treated gel relates to condensed silicon monoxide. The emerging melt protects with a carbon clathrates the interior part of the gel from access of oxygen, and at the same time, the conditions for reducing SiO_2 to SiO are apparently created, whereas in cooling it is condensed.

The preservation of the carbon-containing components in the gel cluster determined the synthesis of boron and silicon

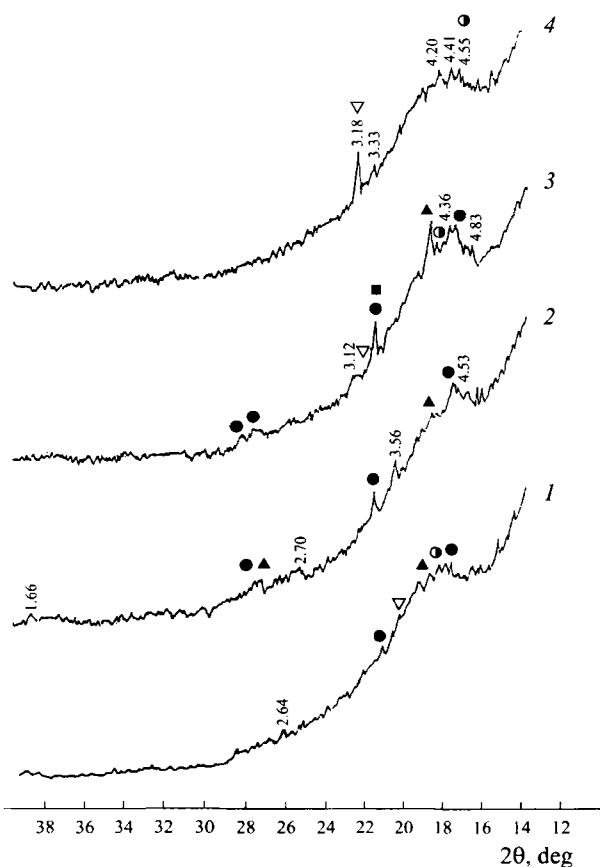


Fig. 4. Diffraction patterns of heat-treated ethyl silicate gel compositions with addition of H_3BO_3 at the temperatures of 1373 K (1) and 1273 K (2–4) in air medium. Quantity of H_3BO_3 additive: 1, 2) 0.2%; 3) 2.0%; 4) 4.0%; ■) quartz; ▲) cristobalite; ●) tridymite; ○) silicon oxynitride; ▽) SiO_2 .

carbides from this material. The development of a reducing medium results in intensification of the synthesis of oxygen-free compounds. Confirmation of this is the presence of B_4C and $\beta\text{-SiC}$ peaks in the diffraction patterns of the composition heat-treated *in situ* at different temperatures.

The beginning of synthesis of B_4C and $\beta\text{-SiC}$ is already observed at the temperature of 773 K (Fig. 5). Additional ev-

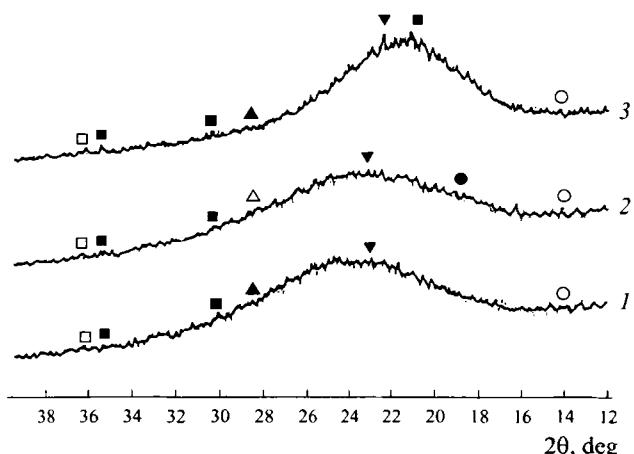


Fig. 5. Diffraction patterns of ETS-32 - H_3BO_3 (2.0%) gel composition heat-treated *in situ* in ambient air: 1) 773 K; 2) 1073 K; 3) B_4C ; ■) $\beta\text{-SiC}$; ○) C; ●) silicon oxynitride; ▽) quartz; △) SiO_2 .

idence of synthesis of silicon and boron carbides from the components of the ETS - H_3BO_3 composition heat-treated at 773 K is the presence of a doublet in the IR spectrum band at 710 and 740 cm^{-1} , which corresponds to Si – C and B – C bonds. However, with an increase in the heat treatment temperature, the intensity of the band at 740 cm^{-1} related to the B – C bond decreases compared to the intensity of the band at 710 cm^{-1} . Consequently, the nano-size boron carbide is more easily oxidized than SiC. Its oxidation at temperatures above 773 K can be accompanied by slight mass loss, since the amount of synthesized boron carbide is probably very low.

The absence of B_4C and $\beta\text{-SiC}$ peaks in the diffraction patterns of the ETS - H_3BO_3 compositions cooled in air after heat treatment (Fig. 4) can be probably accounted for by the fact that the nano-size particles of the newly formed B_4C and $\beta\text{-SiC}$ are easily oxidized in ambient conditions.

According to the petrographic analysis, the particles of the ETS - H_3BO_3 composition after heat treatment at 1273 K (in ambient air) represent a vitreous phase with $n_{av} = (1.450 - 1.458) \pm 0.006$ which contains inclusions of H_3BO_3 and an opaque phase in different ratios. Table 1 characterizes the optical properties of the components and their

TABLE 1

Content of H_3BO_3 , wt.%	Characteristics of components	Component ratio, vol.%
0.2	Clear semitransparent glass, $n_{av} = (1.450 - 1.458) \pm 0.006$, with inclusions of the gas phase (4 μm in size) and opaque particles Brownish gray glass, $n_{av} = (1.450 - 1.458) \pm 0.006$, with inclusions of $\text{B}(\text{OH})_3$ and the opaque particles Opaque inclusions	90 – 95 vitreous phase 5 – 10 opaque phase
2.0	Clear glass, $n_{av} = (1.450 - 1.458) \pm 0.006$, with inclusions of $\text{B}(\text{OH})_3$ and opaque particles $\text{B}(\text{OH})_3$ aggregates (up to 30 μm in size) Opaque particles (up to 20 μm in size)	72 – 70 vitreous phase 1 – 3 $\text{B}(\text{OH})_3$ 20 – 25 opaque phase
4.0	Clear glass, $n_{av} = 1.458 \pm 0.006$, with inclusions of $\text{B}(\text{OH})_3$ and the opaque phase $\text{B}(\text{OH})_3$ aggregates (up to 20 μm in size) Opaque particles (up to 30 μm in size)	45 – 55 vitreous phase 3 – 5 $\text{B}(\text{OH})_3$ 40 – 50 opaque phase

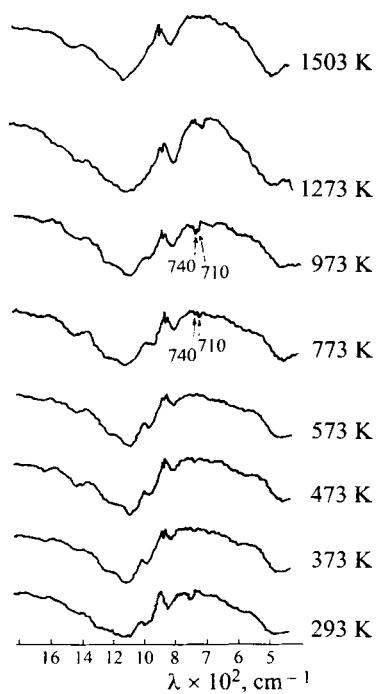


Fig. 6. IR spectra of heat-treated ETS-32 – H_3BO_3 (2.0%) gel compositions.

ratios in the investigated samples. The opaque phase is represented by carbon which was not oxidized in heat treatment. An increase in the content of the H_3BO_3 additive determined an increase in the amount of carbon inclusions in the glass. The carbon part by volume increases from 10 – 25% (0.2% H_3BO_3) to 20 – 25% (2.0% H_3BO_3) or to 40 – 50% (4.0% H_3BO_3). Consequently, introduction of boric acid in ethyl silicate gels delays the thermal destruction of the carbon-bearing binder components in heating of gel even in air at a

temperature above 1173 K. The compositions of ETS – H_3BO_3 were recommended for intensification of synthesis of β -SiC and B_4C in different materials.

The investigated ETS – H_3BO_3 compositions with additives of 0.2 to 4.0% boric acid were used as binders in production of silicon carbide structural materials and corundum-graphite refractories [5.6]. Addition of this composition to the materials not only intensified sintering processes but also contributed to reinforcement of the ceramic matrixes with filamentary formations of β -SiC and B_4C .

Thus, the study of the thermal destruction of ETS – H_3BO_3 composition established favorable conditions for preservation of the carbon-bearing components of the products of ethyl silicate hydrolizate polycondensation in heating and the beginning of synthesis (773) of silicon and boron carbides from the composition components.

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